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Thiolated Carbon Nanotubes/CdSe Quantum Dot Based Hybrid Solar Cells with Improved Long-term Stability

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Abstract. In this work, the development of room-temperature solution-processed hybrid solar cells based on carbon nanotubes (CNT) - CdSe quantum dot (QD) hybrid material incorporated into a layer of conjugated polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)], PCPDTBT, has been demonstrated. Incorporation of multi walled CNTs helps to improve the long-term efficiency of the solar cells in respect of power conversion efficiency (PCE) and short-circuit current density (Jsc) compared to QD only based devices. For the formation of the hybrid material hexadecylamine (HDA)/ trioctylphosphine oxide (TOPO) capped CdSe QDs were attached to CNTs by engineering the interface between CNTs and CdSe QDs by introducing thiol functional groups to CNTs. Initial PCE values of about 1.9 % under AM1.5G illumination have been achieved for this hybrid CNT-CdSe photovoltaic device. Furthermore, the long term stability of the photovoltaic performance of the devices was investigated and found superior to CdSe QD only based devices. About 90 % of the original PCE remained after storage in a glove box for almost one year without any further encapsulation. It is assumed that the improvement is mainly due to the thiol-functionalization of the CNT interface leading to a strong binding of CdSe QDs and a resulting preservation of the nanomorphology of the hybrid film over time.

Introduction

Solution-processed solar cells based on organic–inorganic hybrid materials have been developed as an alternative route towards low-cost fabrication, high efficiency, light-weight and flexible large-area devices [1]. Hybrid solar cells are very similar to that of organic solar cells; the only difference is that inorganic semiconductor QDs are used as electron acceptors instead of PCBM (or other fullerene derivatives) [2]. The QDs surface ligands [3] and the photovoltaic device architecture [4] are important factors in determining the optoelectronic properties of QD solar cells. Recent improvement in QD solar cell power conversion efficiencies up to 5.5 % were based on Polymer/PbSxSe1-x alloyed QDs which showed improved PCEs compared to both conventional PbS or PbSe QDs based devices [5]. However, solar cells based on solution-processed hybrid materials reported thus far generally suffer from a poor device long-term stability in air [6]. Hence, simultaneously achieving the goals of high efficiency, solution-processability and long-term stability in hybrid photovoltaic devices remains a major challenge. Especially the aspect of device stability has been given relatively little consideration and attention so far [7].

The limitation in electron conductivity and mobility for hybrid solar cells is mainly related to the not optimized nanomorphology of the hybrid photoactive film resulting from the nanophase separation of the donor and acceptor phases during solvent evaporation and annealing of the film. Hence, the design of a more continuous electron-transport pathway combined with environmental stability should greatly enhance the performance of hybrid solar cells. In this context, carbon-based

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materials such as CNTs and graphene, are ideal organic compounds to be combined with inorganic semiconductor QDs. CNTs posses excellent environmental stability and high charge mobilities, which could be utilized to overcome the low electron mobilities in hybrid solar cells [8, 9]. There have been already some efforts to incorporate CNTs into solar cells, for example as a hole extraction layer [10, 11], and as charge transport layer or electrode [9, 12]. So far, only a relatively low PCE of 0.7 % has been reported for CNTs incorporated into the active layer of hybrid solar cells [13]. The integration of QD-graphene nanocomposites into such hybrid solar cells has been recently realized showing a significant improvement in PCE compared to QD-only based devices [14].

The preparation of CNT-QDs hybrid materials is usually based on the simple addition of QDs to CNTs, utilizing solely Van der Waals interactions between QDs and the surface of the CNTs [15]. Nevertheless, this method tends to result in uncontrolled QD loading. Using in-situ synthesis of semiconductor nanoparticles directly on the surface of CNTs might be considered as an alternatives route. However, this route was found to interfere with the QD synthesis leading to non-uniform and polydisperse nanocrystals [16, 17].

In this work, we apply a simple synthesis method towards thiol-functionalized CNTs recently reported for the thiolation of reduced graphene-oxide [14, 18]. The successful incorporation of a novel hybrid materials based on CdSe QDs bound to thiolated CNTs into active layers of hybrid solar cells is reported. This method demonstrates a promising potential path towards air-stable high-performance solution-processed hybrid solar cells.

Experimental

CdSe QD synthesis. The CdSe QDs were synthesized according to Yuan et al [19]. First, 2898 mg (12 mmol) of HDA (hexadecylamine, 95%, Merck Schuchardt), 3092 mg (8 mmol) of TOPO (trioctylphosphine oxide, 99%, Sigma-Aldrich), and 444 mg (0.4 mmol) of Cd-stearate were heated up in a nitrogen atmosphere inside a 25 ml three neck flask to 300 °C. After reaching 300 °C, 400 ml (0.4 mmol) of a 1 M solution of selenium in TOP (trioctylphosphine, 97%, ABCR) was rapidly injected. The synthesis was continued under stirring 1000 rpm and stopped after 30 min. QDs with full width at half maximum (FWHM) value of 24.5 nm, first excitons absorption peak about 625 nm, PL peak at wavelength 645 nm, and average size 6 nm have been achieved.

CNT thiolation. Thiolated CNTs were achieved according to a procedure reported in literature [18, 20]. In brief, pristine multiwalled CNTs (Baytubes, Bayer Material Science) were sonicated for 24 hours at 70 °C in a mixture of concentrated HNO_3 and H_2SO_4 with the volume ratio of 3:1. Afterwards the treated CNTs were intensively washed with water. Afterwards, CNTs were thiol-functionalized by a procedure reported previously [14, 18]. CNTs were refluxed with phosphorus pentasulfide (P_4S_{10}) in DMF (dimethylformamide, ≥99.8%, Carl Roth) and heated up to 120 °C in a vacuum for 24 hours. The black thiolated CNT product was collected by filtering with a Whatman NL 16 polyamide 0.2 μm membrane. Subsequently, a washing procedure of the CNTs was conducted by soaking of the material in 150 ml DMF for 30 min. Afterwards DMF was removed by applying vacuum filtration. The same procedure was repeated three times to further purify the product. Thiolated CNTs were then re-dispersed in DMF and homogenized in an ultrasonic bath until a stable dispersion was formed. Finally thiolated CNTs with an average length of 357 nm were obtained.

CNT–CdSe QD hybrid formation. 1.6 mg CDSe QDs, were dissolved in 4.9 ml hexanoic acid and stirred for 22 min at 110 °C in order to reduce the amounts of ligands [21]. 9.8 ml Methanol was then added to the solution and stirred for another 11 min. Separation of QDs was conducted by centrifuging the dispersion for 1 min at 14.5 krpm. Afterwards, chloroform and methanol were added to precipitate the QDs again in order to remove the residual acid. After being recovered by centrifugation, the QDs were finally dispersed into chlorobenzene (CB) at a certain concentration. For 1 mg of CdSe QDs, 40 μl of <50 μg ml−1 CNT dispersion in DMF was taken and centrifuged in a 2 ml centrifugation tube for 3 min. Afterwards, the DMF solution was carefully removed by centrifugation. Finally, the CdSe QDs/CB solution was added into the centrifugation tube with the collected thiolated CNTs inside, resulting in a 400: <1 weight ratio of CdSe QDs:CNT and shaked for 45 seconds at RT at the maximum speed using a vortex mixer.

Solar cell manufacturing. Thiolated-CNT–CdSe QD/PCPDTBT hybrid solar cells were fabricated and compared to CdSe QD/PCPDTBT solar cells which served as reference. In order to identify the effect of thiol functionalizaton on device performance specifically, the physical mixture of non-thiolated CNTs-CdSe QD/PCPDTBT hybrid solar cells were also fabricated for comparison. The final ink was spun cast using a WS400-6NPP-Lite spin coater from Laurell Technologies at 800 rpm for 30 s followed by a 60 s drying step at 1800 rpm, resulting in an active layer thickness of about 80 nm. The spin coating was done on a structured ≤10 Ωsq ITO substrate from Präzisions Glas & Optik GmbH, that was treated for 5 min with oxygen plasma before Baytron AI4083 PEDOT:PSS from HC Starck was spin coated at 3000 rpm for 30 s and dried afterwards for 25 min at 145 °C, to form a 70 nm thick hole blocking layer. After thermal evaporation of an 80 nm aluminum layer the solar cells were annealed at 145 °C for 5 min. Afterwards, they were placed in a glove box under nitrogen atmosphere without any further encapsulation.

Characterization. TEM was performed on a Jeol JEM2100F electron microscope (Jeol Ltd., Tokyo, Japan) operated at 200 kV. UV–Vis absorption spectra were obtained using a TIDAS 100 J&M diode-array spectrometer (Spectralytics, Aalen, Germany). Current density versus voltage (J–V) characteristics were measured by a computer-controlled Keithley 2400 source meter measurement system under 100 mW/cm2 illumination with an AM1.5G filter.

Results and discussion

Thiolated CNTs decorated with CdSe QDs were obtained according to a procedure reported in literature [19] and is described in the experimental section. The QDs are attached to the CNT via thiol-binding. TEM images (see Fig. 1) show the dense QD loading on CNTs.

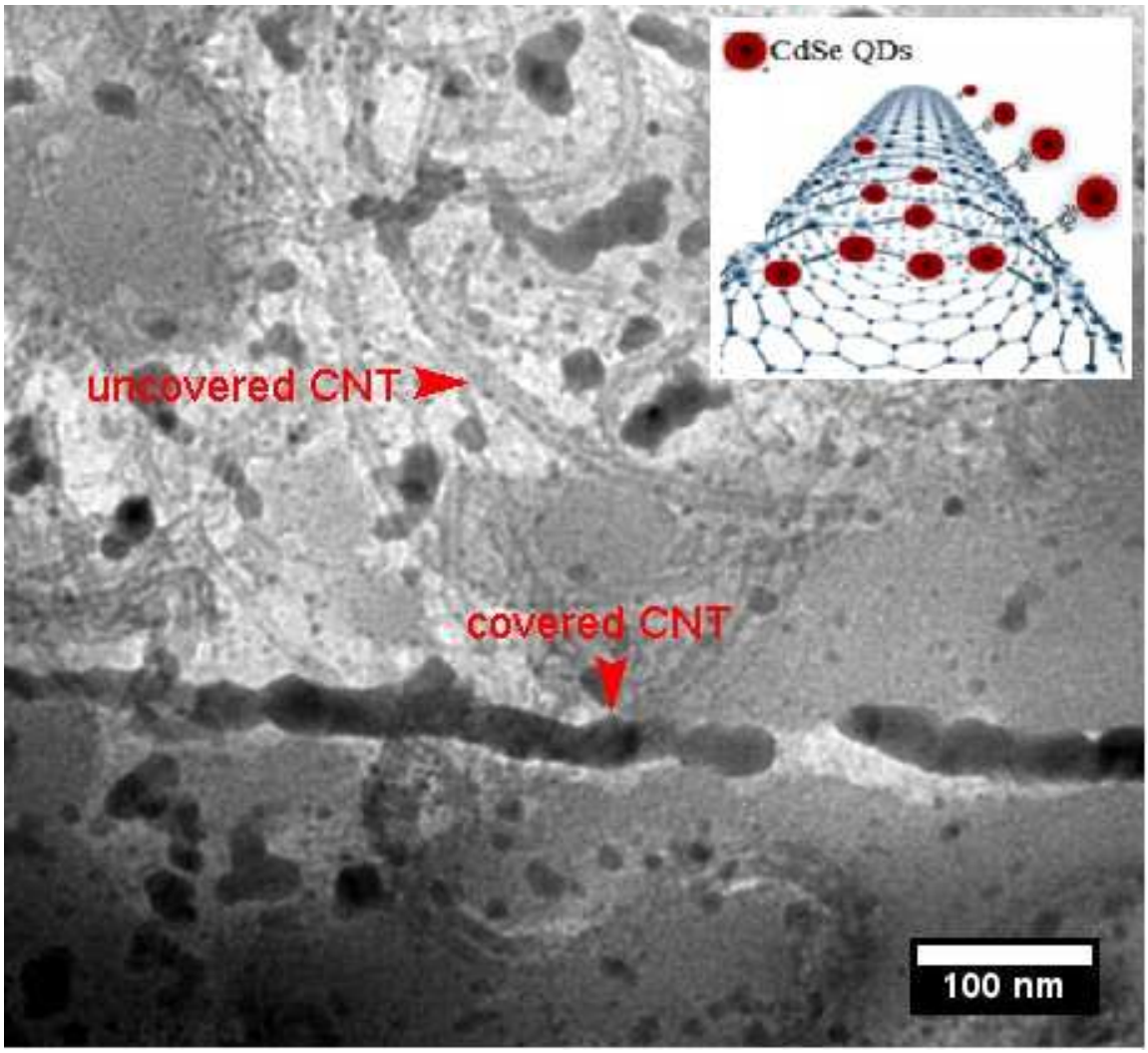

Fig. 1. TEM image of CNTs decorated with CdSe QDs. The inset shows a schematic of the CNT-CdSe QDs hybrid material in comparison with uncovered CNTs.

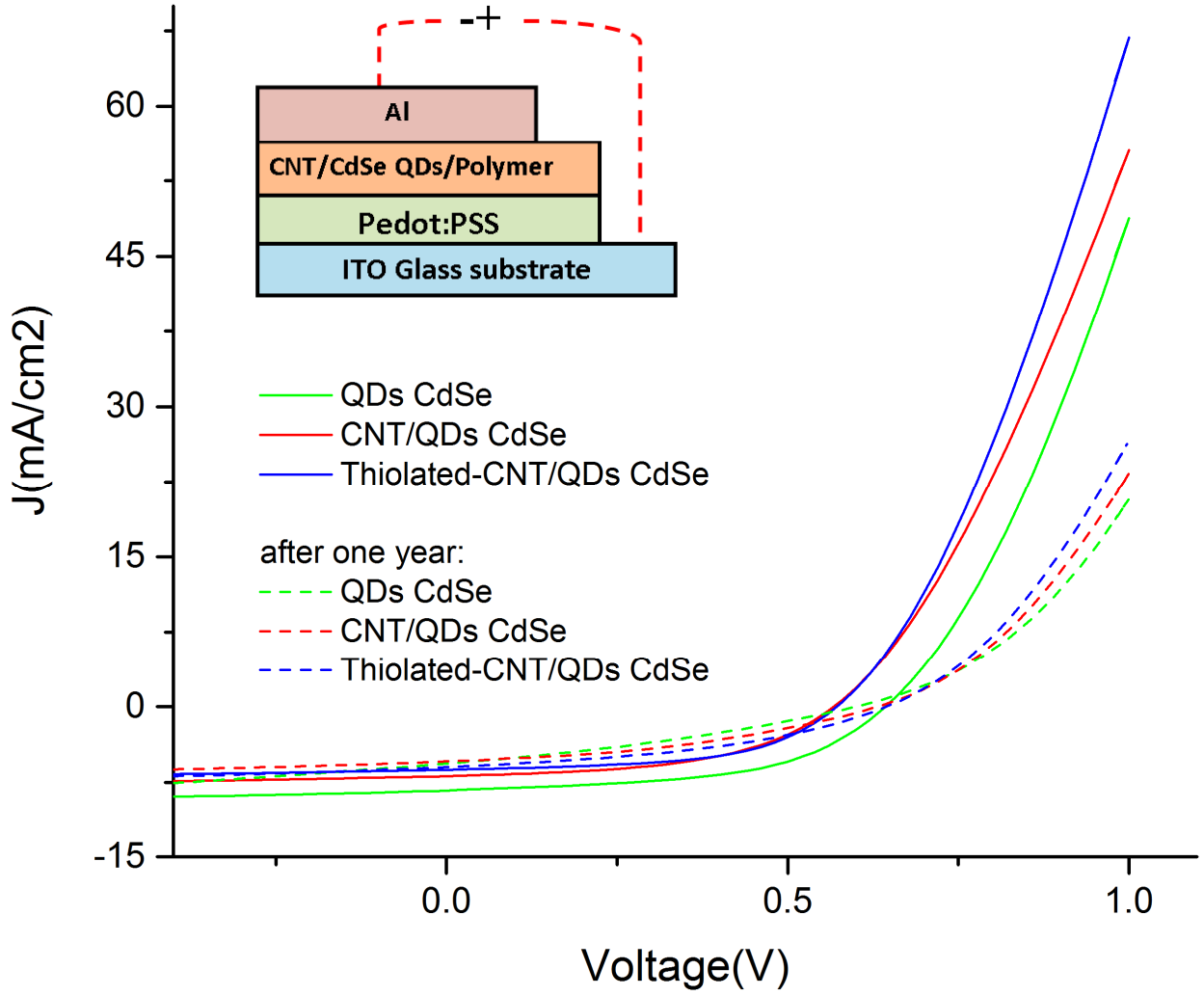

Fig. 2 Current-density voltage curves of hybrid solar cells based on CdSe QDs, CNT–CdSe QDs and thiolated CNT–CdSe QDs. The inset shows a schematic of the solar device structure

Solar cells were prepared according to the description given in the experimental section. The photovoltaic device architecture of the utilized solar cells is depicted schematically in the insert image of Fig. 2. From the data visualized in Fig. 2, one can extract, that after one year storage, the largest drop in device PCE is observed for CdSe based hybrid solar cells, followed by CNT–CdSe QD based devices for and thiolated CNT–CdSe QD based devices, which are 60%, 23% and 10 % respectively. Further solar cell parameters of freshly prepared devices and devices measured after one year storage listed in Table 1 .

Table 1 Comparison of solar cell performances of freshly prepared solar cells and after their storage for one year.

	Fresh cells					After one year storage					Loss of PCE [%]	Increasing Rs (%)	Decreasing Jsc (%)	FF Reducing (%)
	Voc [V]	Jsc [mA/cm^2]	FF	PCE [%]	Rs (Ω)	Voc [V]	Jsc [mA/cm^2]	FF	PCE [%]	Rs (Ω)				
CdSe QDs	0.64	8.31	0.6	2.81	9.7	0.62	5.59	0.34	1.13	17	59.95	75.26	32.7	38.2
CNT/ CdSe QDs	0.56	6.2	0.5	1.85	10	0.61	5.94	0.39	1.43	14.2	23.12	40.59	4.2	27.8
Thiolated -CNT/ CdSe QDs	0.58	5.78	0.6	1.88	8	0.66	5.71	0.45	1.69	9.5	9.89	18.75	1.2	19.6

The results presented in Table 1 show that the initial PCE values of differently composed hybrid solar cells, both from freshly prepared cells and from cells stored for one year under nitrogen atmosphere. An initial PCE of about 1.9 % was reached for thiolated CNT/CdSe QDs based solar cells. The physical mixture of CNTs and CdSe QDs resulted in similar initial efficiencies. However, in comparison CdSe QDs based solar cells as reference solar cells resulted in initial efficiencies of 2.8 %. Although all of the freshly prepared cells have similar value in fill factor, it can be clearly seen that a higher Voc and Jsc contributed significantly to higher PCEs.

Comparison of the PCE values between freshly manufactured devices and devices stored for one year can be considered as a simple way for determining one aspect of long-term stability of solar cells. The loss of PCE from three different device types was investigated over time. A total of loss of 60 % in PCE was recorded for CdSe based solar cells whereas CNT/CdSe QDs solar cells lost 23 % of their initial PCE. In comparison thiolated CNT/CdSe QDs solar cells exhibited only a loss in PCE of about 10%. A decreasing Jsc after one year of storage has been observed for all solar cells. CdSe QD based solar cells show a 33 % drop from its initial Jsc. Surprisingly, both CNT/CdSe QD and thiolated CNT/CdSe QD based devices showed only Jsc losses of 4.2 % and 1.2 % respectively. A total of loss of 38 % of the initial fill factor (FF) has been observed for CdSe based solar cells, whereas CNT/CdSe QD and thiolated CNT/CdSe QD based cells showed a total of loss of 28% and 20 % from its initial FF respectively. We conclude that chemical attachment between thiolated CNT and CdSe QDs improves the long-term stability of solar cell parameters such as FF and Jsc and retards the increase of series resistantances. We assume that a better preservation of the initial nanomorphology for the thiolated CNT-QD based solar cell occur and de-attachement of QDs is slowed down significantly compared to the non-functionalized CNT based solar cells. Further investigations are currently underway to clarify these assumptions.

Summary and Conclusion

A significant improvement in long-term stability of solar cell parameters by incorporating thiolated CNT-CdSe QDs hybrid materials instead solely QDs into the photoactive layer of hybrid polymer solar cells has been obtained. The best long-term stability was obtained from thiolated CNT-CdSe QDs, where about 90 % of the original PCE remained after storage in a glove box for almost one year without any further encapsulation. Moreover, almost no lost in current density during storage was observed. This results show that thiolated CNT-QDs nanocomposites are suitable acceptor materials for photovoltaic applications. Further research is needed to fully exploit their potential and engineer optimized CNT-QDs based solar cells.

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